

Vapor Pressure and Critical Point of Tritium Oxide

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A simple general corresponding-states principle has been developed to represent the vapor pressure of tritium oxide from its triple point to its critical point, to describe the available experimental data, and to extrapolate beyond their range. This work takes advantage of the adoptions of the ITS-90 temperature scale and of the new critical parameters obtained from the extended corresponding-states principle. The vapor pressure data are described within their scatter in the entire temperature range. Comparisons with the available experimental data show that the extended corresponding-states principle for vapor pressure can calculate values with good accuracy. The substance-dependent characteristic parameters are given, such as critical temperature, critical density, critical pressure, and acentric factor. The values of the pressures, along with their first and second derivatives, as a function of temperature over the entire region from the triple point to the critical point are tabulated and recommended for scientific and practical uses. © 2003 American Institute of Physics. [DOI: 10.1063/1.1565352]

Key words: boiling point; corresponding-states principle; critical density; critical parameters; critical pressure; critical temperature; ITS-90; triple point; tritium oxide; vapor pressure.

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1. Introduction

Reliable data on the thermophysical properties of tritium oxide (T₂O) are needed for designing and operating fusion reactors. Since available experimental information on the thermophysical properties of T₂O is quite limited, prediction must be made with the aid of various theoretical methods such as the corresponding-states principle. Popov and Tazetdinov¹ and Jones² measured the vapor pressures for temperatures from the triple point up to 368 and 387 K, respectively. There are no reported experimental data from 387 K up to the critical point for T₂O. Matsunaga and Nagashima³ published in 1986 what was then the best prediction for its vapor pressure from the triple point to the critical point (using the corresponding states principle, similarities between H₂O, D₂O and T₂O). Harvey and Lemmon⁴ have recently published the vapor pressure of heavy water (D₂O) from the triple point to the critical point, whereas Wagner and Pruss have evaluated the data on water.^{6,16}

Subsequent advances include: a new representation of the thermodynamic temperature scale, known as ITS-90,⁵ was adopted as the new international standard in 1990, a standard correlation for the vapor pressure of ordinary water has been produced on ITS-90 by Wagner and Pruss,⁶ and a simple general corresponding-states principle that can be applied to highly nonspherical substances was recently developed by

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Xiang.⁷⁻⁹ This corresponding-states approach was shown to be applicable to all substances and it is applied here to T₂O.

2. Present Method

2.1. Vapor-Pressure Equation

To represent the experimental data over the entire range from the triple point to the critical temperature, the vapor-pressure curve was based upon an equation with known physical behavior and has three substance-dependent parameters as described in the Xiang-Tan equation¹⁰

$$\ln p_r = (a_0 + a_1 \tau^{n_1} + a_2 \tau^{n_2}) \ln T_r, \quad (1)$$

where $\tau = 1 - T_r$; the reduced temperature, $T_r = T/T_c$; the critical temperature, T_c ; the reduced pressure, $p_r = p/p_c$; and the critical pressure, p_c . The value of n_1 is 1.89 and the value of n_2 is $3n_1$ or 5.67. The substance-dependent parameter a_0 is the Riedel parameter¹¹ and a_1 and a_2 are substance-dependent parameters. The functional form presented in Eq. (1) is rewritten as

$$p_r = \exp[(a_0 + a_1 \tau^{n_1} + a_2 \tau^{n_2}) \ln T_r] \quad (2)$$

and

$$p = p_c \exp[(a_0 + a_1 \tau^{n_1} + a_2 \tau^{n_2}) \ln T_r]. \quad (3)$$

The slope of the vapor-pressure equation is given by

$$dp/dT = \frac{d \ln p_r}{dT_r} p/T_c, \quad (4)$$

where

$$\begin{aligned} \frac{d \ln p_r}{dT_r} &= (a_0 + a_1 \tau^{n_1} + a_2 \tau^{n_2})/T_r \\ &\quad - (n_1 a_1 \tau^{n_1-1} + n_2 a_2 \tau^{n_2-1}) \ln T_r \end{aligned} \quad (5)$$

At the critical point, $d \ln p/d \ln T = \alpha_c$ is the Riedel parameter.

The second derivative of pressure as a function of temperature is given by

$$d^2 p/dT^2 = \left[\frac{d^2 \ln p_r}{dT_r^2} + \left(\frac{d \ln p_r}{dT_r} \right)^2 \right] p/T_c^2 \quad (6)$$

where

$$\begin{aligned} \frac{d^2 \ln p_r}{dT_r^2} &= [n_1(n_1-1)a_1 \tau^{n_1-2} + n_2(n_2-1)a_2 \tau^{n_2-2}] \ln T_r \\ &\quad - (a_0 + a_1 \tau^{n_1} + a_2 \tau^{n_2})/T_r^2 \\ &\quad - 2(n_1 a_1 \tau^{n_1-1} + n_2 a_2 \tau^{n_2-1})/T_r. \end{aligned} \quad (7)$$

Equation (1) can be used to extrapolate precise vapor pressure measurements at modest pressures to the critical point and to the triple point, provided that the critical temperature is known. When the temperature approaches the critical point, the second derivative should weakly approach infinity, which becomes significant only near several thousandth of τ .

TABLE 1. General coefficients of the extended corresponding-states principle for vapor pressure in Eq. (9)

a_{00}	5.790 206	a_{10}	6.251 894	a_{20}	11.658 59
a_{01}	4.888 195	a_{11}	15.085 91	a_{21}	46.782 73
a_{02}	33.911 96	a_{12}	-315.024 8	a_{22}	-1672.179

For this case, the amplitude of the leading-order nonanalytic term in Eq. (6) is not consistent with the correct universal constant.

2.2. The Extended Corresponding-States Principle

The two-parameter corresponding-states method can only be applied accurately to spherical molecules, e.g., argon, krypton, and xenon. In order to extend the corresponding-states principle to molecular fluids, it is necessary to take into account the nonspherical nature of real molecules through the acentric factor defined by Pitzer *et al.*,¹² which works well for a wide range of nonpolar substances but its predictive capability for polar and associating molecules is generally poor. The use of four parameters for polar fluids corresponds to an intermolecular potential function in which dispersion and dipole-dipole interaction effects are accounted for. To extend the corresponding-states principle of Pitzer *et al.* to highly nonspherical substances, the recently developed extended corresponding-states parameter, $\theta = (Z_c - 0.29)^2$, is introduced to describe the deviation of the critical compression factor, Z_c , of a real nonspherical molecule from spherical molecules.⁷⁻⁹ For spherical fluids $Z_c = 0.29$. The corresponding-states parameter θ is obtained from the parameters of the behavior in the critical state, which are effected by the dipole and quadrupole moments. The extended corresponding-states parameter θ reflects the physical behavior displayed by the dipole and quadrupole moments. The extended corresponding-states parameter measures the behavior of the deviation of a highly nonspherical molecule

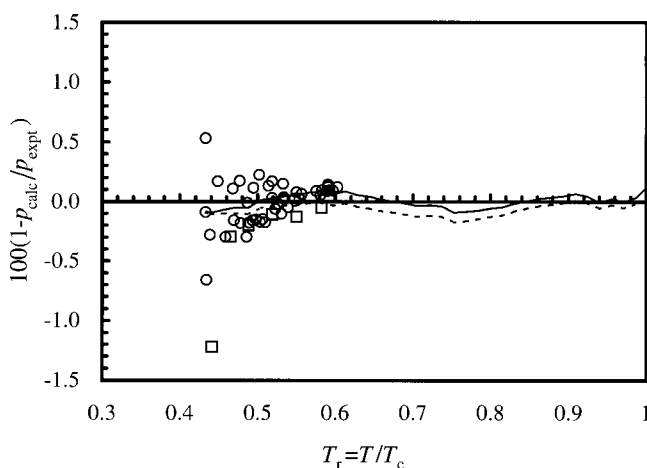


FIG. 1. Comparison of the experimental vapor-pressure data for T₂O with values calculated from the extended corresponding-states principle: (□) Popov and Tazetdinov; (○) Jones; (—) Matsunaga and Nagashima (ITS-90); (---) Matsunaga and Nagashima (original).

TABLE 2. The critical parameters, acentric factor, and three substance-dependent parameters for tritium oxide in the Xiang–Tan equation obtained from extended corresponding states given in Eq. (9)

T_c (K)	641.657	a_0	7.708 519
p_c (kPa)	21 385	a_1	10.875 29
ρ_c (mol dm ⁻³)	17.1	a_2	23.847 70
ω	0.371	θ	$3.090\ 3 \times 10^{-3}$
T_{triple} (K)	277.64	p_{triple} (kPa)	0.662 9
T_b (K)	374.66		

from that of the spherical molecule argon, as is similar in the definition of the acentric factor. The relation between the critical compression factor and acentric factor, $Z_c = 0.29 - 0.08\omega$,^{12,13} is only approximate for nonpolar substances and cannot be applied to highly nonspherical substances. It should be noted that the extended corresponding-states parameter θ is independent for a real molecule, which significantly improves the extended corresponding states behavior of polar substances. It may be deduced that the extended

corresponding-states principle corresponds to adding a quadratic term $0.0064\omega^2$ to the theory of Pitzer *et al.* for normal fluids.

The extended corresponding-states principle for vapor pressure was developed as follows:

$$\ln p_r = \ln p_r^{(0)} + \omega \ln p_r^{(1)} + \theta \ln p_r^{(2)}, \quad (8)$$

where the acentric factor,¹² $\omega = -1 - \log p_r|_{T_r=0.7}$ and the aspherical factor,⁷⁻⁹ $\theta = (Z_c - 0.29)^2$ are corresponding-states parameters, here $Z_c = p_c / R \rho_c T_c$ is the critical compression factor and $R = 8.314\ 472\ \text{J mol}^{-1}\ \text{K}^{-1}$ is the molar gas constant recommended by Mohr and Tayler.¹⁴

To predict the vapor pressure from the corresponding-states principle, the proper reference equation must be selected which is valid from the triple point to the critical point. Equation (1) fulfills this requirement in that it can be used effectively to correlate and extrapolate the vapor-pressure behavior of simple, nonpolar, polar, hydrogen bond-

TABLE 3. Smoothed pressures, along with their first and second derivatives, as a function of temperature for tritium oxide

T (K)	p (kPa)	dp/dT (kPa/K)	d^2p/dT^2 (kPa/K ²)	T (K)	p (kPa)	dp/dT (kPa/K)	d^2p/dT^2 (kPa/K ²)
277.64	0.66297	4.86E-02	0.3164E-02	458.15	1122.4	25.64	0.4593
278.15	0.68824	5.03E-02	0.3255E-02	463.15	1256.5	28.01	0.4882
283.15	0.98427	6.90E-02	0.4273E-02	468.15	1402.8	30.52	0.5178
288.15	1.3876	9.34E-02	0.5535E-02	473.15	1562.0	33.19	0.5483
293.15	1.9300	0.1248	0.7081E-02	478.15	1734.9	36.01	0.5796
298.15	2.6500	0.1648	0.8954E-02	483.15	1922.3	38.99	0.6116
303.15	3.5947	0.2150	0.1120E-01	488.15	2125.0	42.13	0.6445
308.15	4.8201	0.2774	0.1386E-01	493.15	2343.9	45.43	0.6781
313.15	6.3929	0.3543	0.1698E-01	498.15	2579.6	48.91	0.7126
318.15	8.3911	0.448	0.2061E-01	503.15	2833.2	52.56	0.7479
323.15	10.906	0.5613	0.2480E-01	508.15	3105.5	56.39	0.7841
328.15	14.042	0.6971	0.2960E-01	513.15	3397.4	60.40	0.8213
333.15	17.919	0.8584	0.3505E-01	518.15	3709.8	64.60	0.8594
338.15	22.674	1.049	0.4119E-01	523.15	4043.8	69.00	0.8986
343.15	28.461	1.272	0.4808E-01	528.15	4400.1	73.59	0.9390
348.15	35.450	1.531	0.5574E-01	533.15	4780.0	78.39	0.9807
353.15	43.835	1.830	0.6422E-01	538.15	5184.4	83.40	1.024
358.15	53.828	2.174	0.7355E-01	543.15	5614.4	88.63	1.068
363.15	65.660	2.567	0.8376E-01	548.15	6071.1	94.08	1.114
368.15	79.589	3.013	0.9488E-01	553.15	6555.6	99.78	1.162
373.15	95.892	3.518	0.1069	558.15	7069.2	105.7	1.212
374.66	101.32	3.682	0.1108	563.15	7613.1	111.9	1.265
378.15	114.87	4.084	0.1199	568.15	8188.7	118.4	1.320
383.15	136.85	4.719	0.1339	573.15	8797.2	125.1	1.377
388.15	162.18	5.425	0.1489	578.15	9440.2	132.1	1.438
393.15	191.23	6.209	0.1648	583.15	10119	139.5	1.502
398.15	224.40	7.075	0.1817	588.15	10836	147.2	1.569
403.15	262.12	8.028	0.1996	593.15	11591	155.2	1.641
408.15	304.83	9.073	0.2186	598.15	12388	163.6	1.718
413.15	353.01	10.21	0.2384	603.15	13228	172.4	1.799
418.15	407.15	11.46	0.2593	608.15	14113	181.6	1.887
423.15	467.77	12.81	0.2811	613.15	15044	191.3	1.980
428.15	535.43	14.27	0.3039	618.15	16026	201.4	2.081
433.15	610.68	15.85	0.3276	623.15	17059	212.1	2.190
438.15	694.13	17.55	0.3522	628.15	18148	223.3	2.307
443.15	786.38	19.37	0.3777	633.15	19293	235.2	2.435
448.15	888.07	21.33	0.4040	641.66	21385	256.9	2.686
453.15	999.87	23.41	0.4312				

ing, and associating compounds. Therefore, the corresponding-states method can be used to represent vapor pressures over the entire range as

$$\begin{aligned}\ln p_r^{(0)} &= (a_{00} + a_{10}\tau^{n_1} + a_{20}\tau^{n_2}) \ln T_r, \\ \ln p_r^{(1)} &= (a_{01} + a_{11}\tau^{n_1} + a_{21}\tau^{n_2}) \ln T_r, \\ \ln p_r^{(2)} &= (a_{02} + a_{12}\tau^{n_1} + a_{22}\tau^{n_2}) \ln T_r.\end{aligned}\quad (9)$$

The general coefficients a_{ij} of Eq. (9), given in Table 1, were found from fitting the vapor–pressure data for argon, the weakly nonspherical molecules ethane, propane, difluoroethane, 1,1,1,2-tetrafluoroethane, 1,1-difluoroethane, and the highly nonspherical molecule water. The coefficients are independent of the specific substance and are expected to be universal for all classes of molecules.^{7–9}

3. Experimental Vapor Pressure Data from the Literature

The measurements of Popov and Tazetdinov¹ were on an absolute basis, performed with 98.1% T₂O, while Jones² measured the difference between the vapor pressures of H₂O and 98.6%–99.4% T₂O. The results of both studies were extrapolated to 100% T₂O by the respective authors. The claimed experimental uncertainty was at most 0.4% for Jones' data. The data of Popov and Tazetdinov¹ are estimated to be less reliable. In order to convert the data of Jones² to T₂O vapor pressures, the recently standard correlation for the saturated vapor pressure of H₂O from Wagner and Pruss⁶ was used. All literature data were converted to ITS-90, the temperature scale used throughout this work. No experimental data in the high-temperature region and for the critical parameters have been reported yet.

4. Comparisons and Results

There is agreement between the experimental normal boiling temperature values obtained by Popov and Tazetdinov¹ and by Jones² which are well verified by the calculated values. The experimental data and predicted data from Matsunaga and Nagashima³ are compared with values calculated from the present method as shown in Fig. 1. The experimental data in the high temperature region is needed. The critical parameters, corresponding-states parameters, normal-boiling-point and triple-point temperatures are listed in Table 2. The critical temperature and critical pressure were predicted by Matsunaga and Nagashima.³ The triple-point temperature was taken from Jones.¹⁵ Smoothed pressures, along with their first and second derivatives, as a function of temperature in the range between the triple point and the critical point from the present method are presented in Table 3.

5. Model Uncertainty

Generally speaking, vapor pressures determined by the extended corresponding-states method lie within the experi-

mental uncertainties for the most accurate data since the present method has been extensively tested in previous work.^{7–9} The average deviations between the vapor pressures obtained from the present method [Eq. (9)] and the experimental data are shown in Fig. 1. The uncertainties of the present method were determined to be approximately 0.05%–0.1% in the vapor pressure for substances which have highly accurate experimental data, even in a limited range. The uncertainties are less than 1% for the first derivative and are several percentages for the second derivative according to our mathematical experience.

6. Conclusions

All data included in the previous formulation for T₂O were converted to the ITS-90 temperature scale. The current standard vapor pressure equation for ordinary water^{6,16} was used to convert differential measurements where appropriate. The data obtained by the extended corresponding-states principle are in agreement with the published experimental data and those predicted data within their uncertainties. The uncertainty in vapor pressure of T₂O is estimated at 0.05%–0.1% since the extended corresponding-states principle is used in the present method. The equation of Matsunaga and Nagashima³ does not adequately describe these data because it was based on the IPTS-68 temperature scale. An advantage of the present method is that it allows accurate values to be calculated directly without requiring any temperature conversion. This study also reveals the lack of reported data in the region above 387 K to the critical temperature—additional experimental studies are needed.

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8. References

- ¹M. M. Popov and F. I. Tazetdinov, *At. Energ.* **8**, 420 (1960).
- ²W. M. Jones, *J. Chem. Phys.* **48**, 207 (1968).
- ³N. Matsunaga and A. Nagashima, *Ind. Eng. Chem. Fundam.* **25**, 115 (1986).
- ⁴A. H. Harvey and E. W. Lemmon, *J. Phys. Chem. Ref. Data* **31**, 173 (2002).
- ⁵H. Preston-Thomas, *Metrologia* **27**, 3 (1990).
- ⁶W. Wagner and A. Pruss, *J. Phys. Chem. Ref. Data* **22**, 783 (1993).
- ⁷H. W. Xiang, *Chem. Eng. Sci.* **57**, 1439 (2002).
- ⁸H. W. Xiang, *Int. J. Thermophys.* **22**, 919 (2001a).
- ⁹H. W. Xiang, *J. Phys. Chem. Ref. Data* **30**, 1161 (2001b).
- ¹⁰H. W. Xiang and L. C. Tan, *Int. J. Thermophys.* **15**, 711 (1994).

- ¹¹L. Riedel, Chem. Ing. Tech. **26**, 83 (1954).
¹²K. S. Pitzer, D. Z. Lippmann, R. F. Curl, C. M. Huggins, and D. E. Petersen, J. Am. Chem. Soc. **77**, 3433 (1955).
¹³R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed. (McGraw-Hill, New York, 1987).
¹⁴P. J. Mohr and B. N. Taylor, J. Phys. Chem. Ref. Data **28**, 1713 (1999).
¹⁵W. M. Jones, J. Am. Chem. Soc. **74**, 6065 (1952).
¹⁶W. Wagner and A. Pruss, J. Phys. Chem. Ref. Data **31**, 387 (2002).